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# Nitrogen-Rich Conjugated Microporous Polymers: Facile Synthesis, Efficient Gas storage and Heterogeneous Catalysis

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**Abstract:** Nitrogen-rich conjugated microporous polymers (NCMPs) have attracted great attention in recent years owing to their polarity, basicity, and ability to coordinate metal ions. Herein three NCMPs, structurally close to polyaniline, were facilely synthesized via chemical oxidative polymerization between multi-connected aniline precursors. The NCMPs with high N content (11.84 wt%), intrinsic ultramicroporosity (<1 nm) and moderate surface area (485 m<sup>2</sup> g<sup>-1</sup>), show wide-ranging adsorption functionality, e.g. CO<sub>2</sub> uptake (11 wt%) and CO<sub>2</sub>-selectivity over N<sub>2</sub> (360, 1 bar), 1.0 wt% H<sub>2</sub> storage as well as 215 wt% iodine vapor uptake at ambient pressure. Moreover, these NCMPs act as support for palladium catalysts and can maintain >94% activity in Suzuki–Miyaura coupling reactions after six continuous runs.

**Keywords:** Conjugated microporous polymers, polyaniline, gas storage, catalysis, synthesis

## Introduction

Conjugated microporous polymers (CMPs) with small pores (<2 nm), large surface areas, high chemical stability, low density and reversible redox properties, are of great interest for a variety of applications.<sup>1-3</sup> These porous materials have been widely investigated since discovery in 2007, both for fundamental reasons and because of their potentials for application in areas of gas adsorption,<sup>4</sup> heterogeneous catalysis,<sup>5</sup> and electrochemical energy storage.<sup>6</sup> Over the past decade, various aromatic functional building blocks have been incorporated into CMPs for extended applications such as sensors,<sup>7,8</sup> light harvesting,<sup>9</sup> organic light-emitting diodes,<sup>10,11</sup> and

photocatalysis.<sup>12-14</sup>

The porosity of CMPs is largely determined by their backbone structure, although solvent-templating effects can also contribute.<sup>15,16</sup> Generally, CMPs are synthesized via well-developed transition-metal-catalyzed coupling reactions such as the Suzuki,<sup>9</sup> Yamamoto,<sup>17</sup> Sonogashira,<sup>18,19</sup> and Buchwald-Hartwig reactions.<sup>20,21</sup> Expensive (noble) metal-based catalysts or mediators are however needed for their synthesis. Recently, chemical oxidative polymerizations of carbazole,<sup>22-24</sup> thiophene,<sup>25-27</sup> and pyrrole-based precursors<sup>28,29</sup> have been utilized to generate CMPs, using commonly available iron (III) chloride as the oxidant. Electrochemical polymerization of these precursors has also been used to yield CMP thin films on electrodes.<sup>10,11,26</sup> While oxidative polymerization for CMP generation has mainly focused on carbazole and thiophene-based polymers, to the best of our knowledge, the synthesis of highly cross-linked 3D polyaniline networks with intrinsic microporosity and high N content has rarely been reported, and only performed through the addition of cross-linkers.<sup>30</sup>

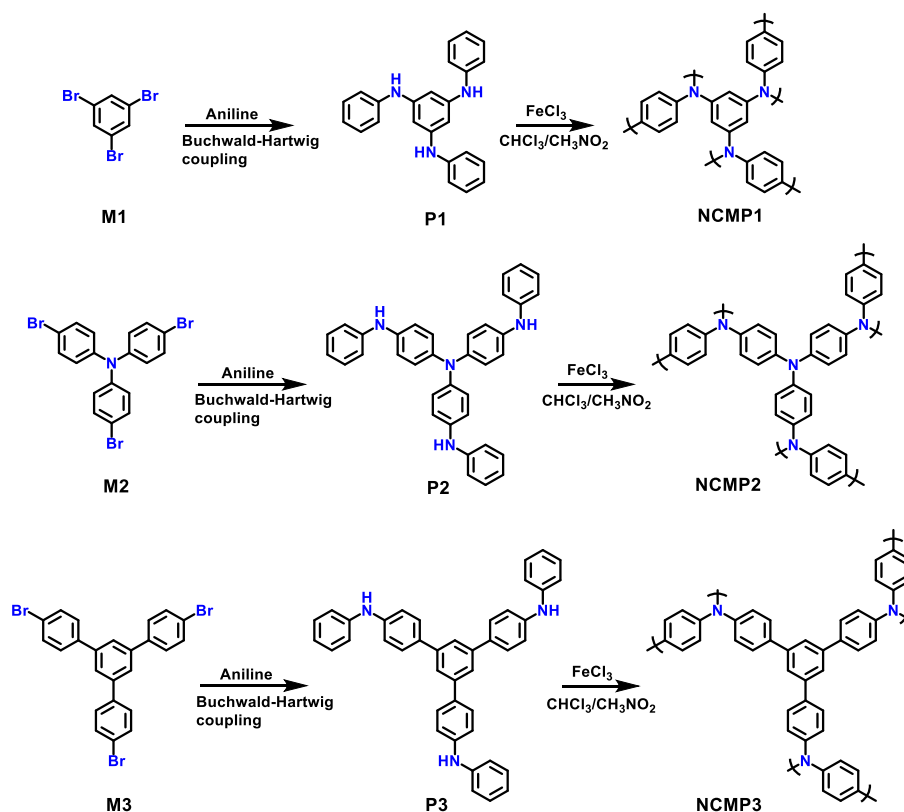
Polyaniline, a prototypical nitrogen-rich conjugated polymer, has emerged as a very important semiconductor that is particularly attractive for electronics and energy storage devices.<sup>31-33</sup> Microporosity introduced to such organic semiconductors may provide desired interface properties, such as interpenetration with a second material, enabling better gas or charge separation, and sensing properties via interactions with the electron pool.<sup>34-36</sup> For example, the incorporation of polyaniline into the porous metal-organic framework MIL-101 could dramatically increase the CO<sub>2</sub>-selective uptake ability owing to the functionality of the nitrogen centers.<sup>36</sup>

Nitrogen-rich conjugated microporous polymers (NCMPs) could furthermore be of interest owing to their polarity, basicity, and ability to coordinate metal ions. Herein we report three NCMPs structurally close to conventional polyaniline, which are synthesized via simple chemical oxidative polymerization of multi-connected aniline precursors. Using this simple technique, we are, for the first time, able to prepare polyaniline-like microporous materials with high nitrogen contents. As-prepared porous materials benefit from the high nitrogen density to obtain materials with good CO<sub>2</sub>/N<sub>2</sub> selectivities, and moderate CO<sub>2</sub>, H<sub>2</sub>, and iodine uptake capacities at ambient pressure. The materials also act as excellent supports for Suzuki-Miyaura reaction catalysts, showing high stability and recyclability. Beyond these areas, such NCMPs might furthermore

open new avenues and enable new possibilities for advanced optoelectronic applications.

## Results and discussion

Three multi-connected aniline precursors (**P1**, **P2**, and **P3**) were synthesized via Buchwald-Hartwig coupling between aniline and the tribromoaryl monomers **M1**, **M2**, and **M3**, respectively (Scheme 1, see a detailed characterization of monomers and polymers, and related discussions in supporting information). Chemical oxidative polymerization of these precursors in chloroform ( $\text{CHCl}_3$ ) was carried out using stoichiometric amounts of  $\text{FeCl}_3$  dissolved in nitromethane ( $\text{CH}_3\text{NO}_2$ ) as the reaction medium. The reactions started immediately, as seen from the rapid formation of black precipitates. After filtration and extensive purification using  $\text{CHCl}_3$ , concentrated  $\text{HCl}$  (35 wt%), and hot water (75 °C), **NCMP1**, **NCMP2**, **NCMP3** products were obtained as brown to dark grey powders (Figure 1a) in nearly quantitative yields, indicating a high degree of polymerization.



Scheme 1 Synthetic route to nitrogen-rich CMP networks (**NCMP1**, **NCMP2**, **NCMP3**).

It is well known that oxidative polymerization of aniline and its *N*-substituted derivatives such as *N*-methylaniline occurs generally *via* head-to-tail coupling of the most negatively-charged N

atoms and unsubstituted C<sub>4</sub> atoms.<sup>37</sup> On the basis of atomic electron populations and spin-density simulations of precursors at a B3LYP/6-31G (*d*) level using Gaussian 09 software<sup>38</sup> (Figs. S1-6 and Tables S1-6, see detailed discussions in supporting information), chemical oxidative polymerization of **P1**, **P2**, and **P3** most probably yielded polymer networks **NCMP1**, **NCMP2** and **NCMP3**, respectively, as shown in Scheme 1 and Figure S7. The Fourier transform infrared (FT-IR) spectra of NCMPs showed that the peaks at ~3380 cm<sup>-1</sup> owing to the stretching vibration of the secondary amine (PhNHPh) became much less intensive, indicating that most of these groups are converted into tertiary amines (Ph<sub>3</sub>N) (Figure S8). Three distinct peaks at 1598, 1498, and 820 cm<sup>-1</sup> originated from the precursors owing to C–N, C=C, and aryl C–H bands,<sup>31-33</sup> respectively, present in all the NCMPs, further suggesting a successful coupling. Further characterization of the chemical composition of the formed NCMPs was confirmed by inductively coupled plasma-atomic emission spectrometry (ICP-AES), energy dispersive X-ray spectroscopy (EDX), solid-state <sup>13</sup>C cross-polarization magic angle spinning nuclear magnetic resonance (<sup>13</sup>C CP/MAS NMR), and ultraviolet-visible/near infrared (UV-Vis/NIR) spectroscopies. ICP-AES and EDX measurements confirmed negligible Fe (0.05-0.07 wt%) and high N contents (7.39-11.84 wt%) in the products after extensive purification. Solid-state <sup>13</sup>C CP/MAS NMR spectra of polymers show two main resonances at ~141 and ~128 ppm, originating from N- and H-substituted benzene rings,<sup>20,21</sup> respectively (Figure 1b). Note that the spectrum of **NCMP3** shows an additional resonance at ~113 ppm, due to the C-substituted benzene rings. Solid-state UV-Vis/NIR spectra of the polymers show a narrow peak at ~320 nm and a broad peak in the range 700-1300 nm (Figure 1c). The observed absorption spectra of **NCMP1** and **NCMP2** are comparable to that of traditional polyaniline, owing to the close resemblance to the molecular structure of polyaniline.<sup>31-33</sup> Compared to **NCMP3**, **NCMP1** and **NCMP2** show much more intensive broad peaks in the 700-1300 nm range, indicating a higher doping level. The Cl atom content of as-synthesized polymers was tested to understand the doping level of the materials. As determined by EDX measurements, **NCMP1**, **NCMP2**, and **NCMP3** still contain 5.6, 4.2, and 1.2 wt% of Cl, respectively. It can be reasoned that the higher Cl content found in **NCMP1** and **NCMP2** are due to the more basic triphenylamine units present. The byproduct of HCl resulted from the chemical oxidative polymerization more readily doped with **NCMP1** and **NCMP2** rather

than **NCMP3**.

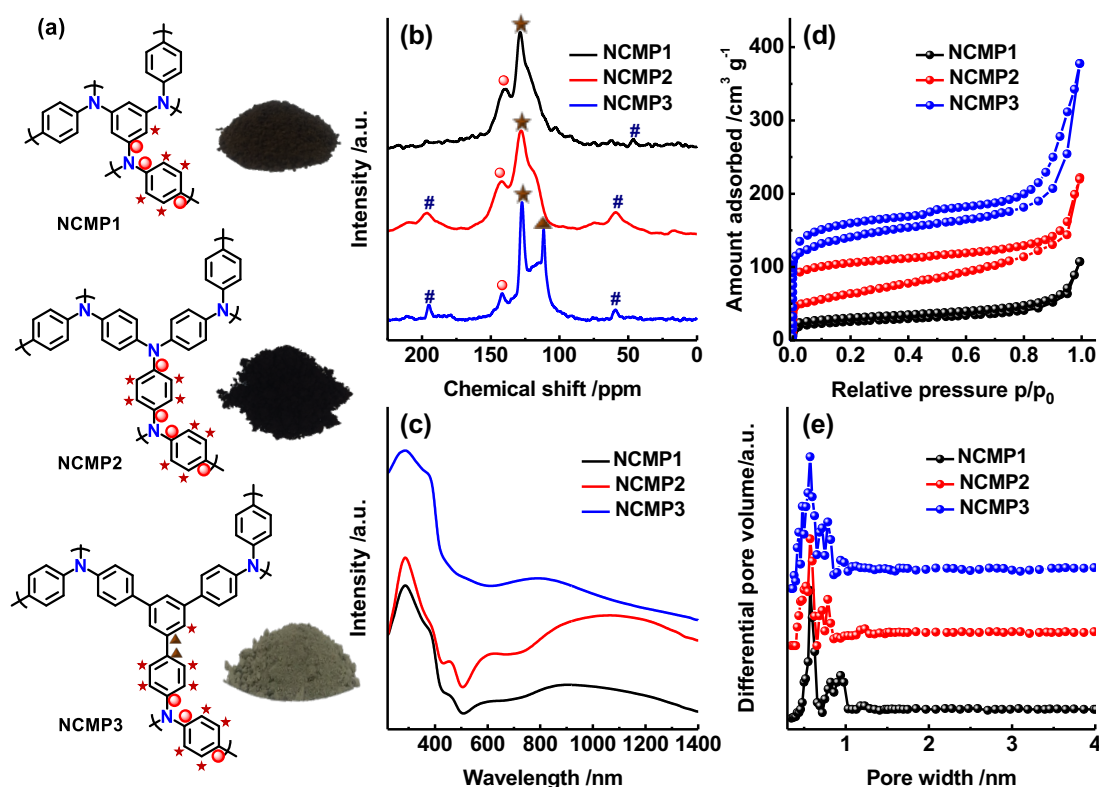


Figure 1 (a) Chemical structures/photographs, (b) solid-state  $^{13}\text{C}$  CP/MAS NMR spectra, (c) UV-Vis/NIR spectra, (d)  $\text{N}_2$  adsorption/desorption isotherms, and (e) pore widths of NCMPs. The symbol # in Figure 1b represents spinning side band.

Scanning electron microscope (SEM) and transmission electron microscope (TEM) images show that the NCMPs consist of aggregated nanoparticles (Figure 2) resulting in some large meso and macropores due to the presence of interstitial voids. High-resolution TEM images also indicate microporous structures. As indicated by thermogravimetric analyses (TGA) carried out in nitrogen (Figure S9), the weight-loss of three polymers at the beginning (0-200  $^{\circ}\text{C}$ ) of the analysis follows the order: **NCMP1** > **NCMP2** > **NCMP3**, which is well consistent with the amount of residual HCl. When heated to 900  $^{\circ}\text{C}$ , the highly cross-linked NCMPs maintained 55-69 wt% carbonaceous residues, which is in contrast to conventional polyaniline yielding no carbonaceous residue.

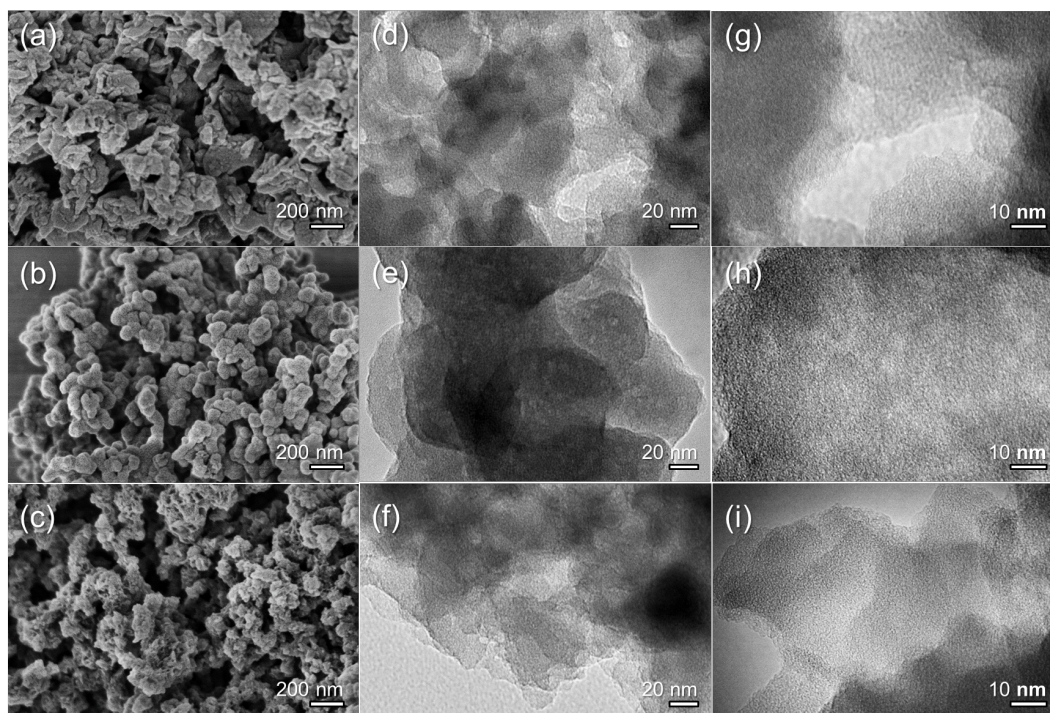


Figure 2 (a-c) SEM and (d-i) TEM images of (a,d,g) **NCMP1**, (b,e,h) **NCMP2** and (c,f,i) **NCMP3** networks at low (d-f) and high (g-i) magnifications.

Microporosity of the NCMPs was confirmed by  $N_2$  adsorption measurements. **NCMP1**, **NCMP2**, and **NCMP3** (Figure 1d) reveal Brunauer–Emmett–Teller (BET) surface areas of 58, 280, and 485  $m^2 g^{-1}$ , total pore volumes of 0.15, 0.30, and 0.57  $cm^3 g^{-1}$  at a relative pressure of  $p/p_0 = 0.994$ , and micropore volumes of 0.06, 0.09, and 0.13  $cm^3 g^{-1}$ , respectively (Table 1). On the basis of the  $N_2$  adsorption isotherms, the NCMPs possess small micropores with sizes below 1 nm as determined by the nonlocal density functional theory (NLDFT) method (Figure 1e).

As discussed above, the NCMP networks mainly consist of the triphenylamine ( $NPh_3$ ) moiety, known as a hole-transporting material for organic electroluminescent devices,<sup>39</sup> as well as an important tecton yielding high surface area CMPs.<sup>21,40,41</sup> Applying our NCMPs for gas storage and as catalytic support is therefore worthy of exploration. All NCMPs exhibit  $CO_2$  storage capability (Figure 3a,b and Table 1), with **NCMP3** showing the highest  $CO_2$  uptake capacity (11 wt%, 2.50  $mmol g^{-1}$ ) at 1 bar and 273 K. The  $CO_2$  uptake capacity obtained is comparable or even superior to that of many porous materials including polyaniline@MIL-101 (<2.26  $mmol g^{-1}$ ),<sup>36</sup> covalent organic frameworks (COF-1, 5, 8, 10, 102, 103 and TpBa, 1.38-2.37  $mmol g^{-1}$ ),<sup>42</sup> and CMPs (CMP-0, 5, TCMP-5, TFM-1, CMP-1- $NH_2$ , CMP-1-COOH, 1.1-2.1  $mmol g^{-1}$ ),<sup>43-45</sup> although it is

lower than that of the optimal CTFs i.e. CTF-0 ( $4.22 \text{ mmol g}^{-1}$ )<sup>46</sup> and CTF-P6M ( $4.17 \text{ mmol g}^{-1}$ )<sup>47</sup> with a much higher N content. Besides the  $\text{CO}_2$  uptake capacity, high  $\text{CO}_2$  selectivity over  $\text{N}_2$  is also a critical factor for real carbon capture applications. Therefore, we measured the  $\text{N}_2$  adsorption of the NCMPs at 273 K to examine their potential ability to separate gases. On the basis of ideal adsorbed solution theory (IAST) calculations (Figure S10, Tables S7,8, see details in supporting information), we found that  $\text{CO}_2$ -selectivities over  $\text{N}_2$  are controlled by the molecular architecture (Figure 3c,d). Two compositions of  $\text{CO}_2/\text{N}_2$  gas mixtures (15/85 and 25/75) were applied for calculation. The results show that the selectivity largely depends on the type of NCMP: **NCMP1**, synthesized from smallest precursor **P1** with the highest nitrogen content (11.84 wt%), shows the highest selectivities with values up to 188 and 360 at 1 bar for the two tested gas mixtures, respectively. The selectivity obtained from **NCMP1** is higher than that of recently reported porous materials such as porous organic polymers (40-78),<sup>48</sup> nitrogen-rich carbons (11-76),<sup>49</sup> and MOFs (93)<sup>50</sup>.

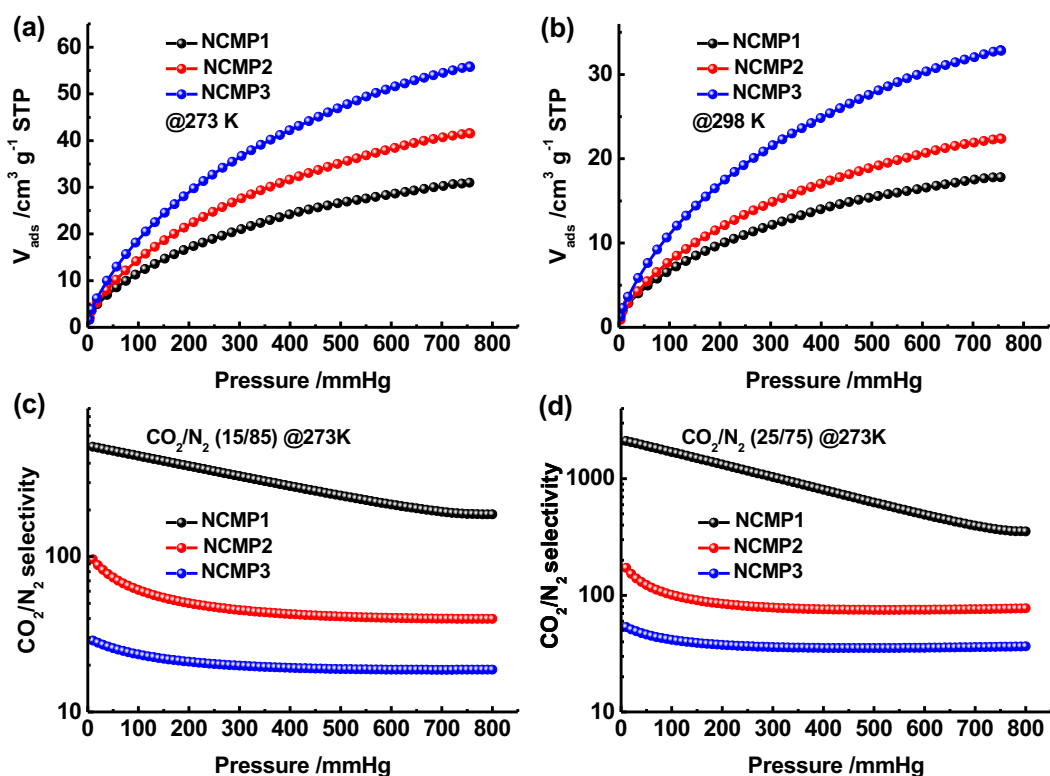


Figure 3 (a,b)  $\text{CO}_2$  adsorption isotherms of NCMPs at 273 and 298 K; (c,d)  $\text{CO}_2$ -selectivities of NCMPs over  $\text{N}_2$  using 15/85 and 25/75 compositions of  $\text{CO}_2/\text{N}_2$  gas phases for calculations.



To explore the interaction between CO<sub>2</sub> and the pore surfaces of the NCMP networks, the isosteric heat of adsorption ( $Q_{st}$ ) was calculated based on the Clausius-Clapeyron equation using single gas adsorption isotherms<sup>51</sup> (Figure S11). Initial  $Q_{st}$  values for CO<sub>2</sub> adsorption were found as high as 33.6, 31.6, and 31.0 kJ mol<sup>-1</sup> for **NCMP1**, **NCMP2**, and **NCMP3**, respectively, which are higher than those values reported for many other porous organic/inorganic adsorbents such as microporous polymer networks (15.6-29.8 kJ mol<sup>-1</sup>),<sup>52</sup> MOFs (15-30 kJ mol<sup>-1</sup>),<sup>53</sup> and carbons (20 kJ mol<sup>-1</sup>)<sup>54</sup>. However, the values remain below the typical energy of chemisorption ( $Q_{st} > 40$  kJ mol<sup>-1</sup>),<sup>55</sup> implying strong physical interactions between adsorbed CO<sub>2</sub> and the functional pore surface. Moreover, the NCMPs show H<sub>2</sub> storage capacities up to 1.02 wt% at 77 K and 1.0 bar (for example, **NCMP3**) (Figure S12), which is higher than the values obtained for most porous polymer networks,<sup>56,57</sup> for example, a recent report on porous hypercrosslinked polymers showed H<sub>2</sub> storage capacities of 1.01 wt% (77 K and 1.13 bar).<sup>57</sup> Again, on the basis of the Clausius-Clapeyron equation,<sup>58</sup> initial  $Q_{st}$  values for H<sub>2</sub> adsorption in **NCMP1** is calculated as high as 8.3 kJ mol<sup>-1</sup> (Figure S13). This value is higher than that of other porous organic polymers such as of PAF-1 (4.6 kJ mol<sup>-1</sup>),<sup>59</sup> PIs (5.3-7.0 kJ mol<sup>-1</sup>),<sup>60</sup> COFs (6.0-7.0 kJ mol<sup>-1</sup>),<sup>61-63</sup> further suggesting a favorable physical interaction between adsorbed H<sub>2</sub> and the porous surface.<sup>64</sup>

Table 1 Summaries of physiochemical properties of NCMPs.

Polymer	$S_{BET}^a$	$V_T^b$	$V_{micro}^c$	N% <sup>d</sup>	CO <sub>2</sub> uptake		H <sub>2</sub> uptake	
					at 1 bar (wt%)		at 1 bar (wt%)	
					273 K	298 K	77 K	87 K
<b>NCMP1</b>	58	0.15	0.06	11.84	6.1	3.5	0.68	0.49
<b>NCMP2</b>	280	0.30	0.09	10.14	8.2	4.4	0.79	0.54
<b>NCMP3</b>	485	0.57	0.13	7.39	11.0	6.5	1.02	0.68

<sup>a</sup>calculated using a multi-point BET method; <sup>b</sup>calculated based on N<sub>2</sub> adsorption at  $p/p_0 = 0.994$ ;

<sup>c</sup>calculated using a MP method; <sup>d</sup>relative content measured by EDX.

In addition to CO<sub>2</sub> and H<sub>2</sub> storage, we also explored the NCMP networks for their potential application in iodine adsorption. Iodine vapor adsorption is of particular interest, since the long-lived radioactive iodine isotopes (e.g. <sup>129</sup>I or <sup>131</sup>I) need to be removed from exhaust fumes of

nuclear power plants regularly.<sup>65</sup> Previous studies showed that nitrogen-containing CMPs are promising to address this issue.<sup>20</sup> Upon exposure to iodine vapor at 1 bar and 358 K, porous NCMPs became gradually darker as iodine molecules diffused into the porous networks. Equilibrium adsorption is found to be 215, 186, and 161 wt% for **NCMP1**, **NCMP2**, and **NCMP3**, respectively. It is well known that electron-deficient iodine (acceptor) interacts with electron-rich adsorbents (donor), giving rise to charge transfer from the HOMO of the donor to the LUMO of the acceptor. Previous studies suggest that the charge-transfer interactions are responsible for the high iodine adsorption capacity of aniline-linked hexaphenylbenzene-based conjugated microporous polymer (HCMP) adsorbents.<sup>20</sup> The NCMPs showed a slightly smaller main pore size than the molecular diameter of iodine (0.57 vs. 0.60 nm), as determined by the nitrogen adsorption isotherms at 77 K. We believe that the combination of nitrogen content and HOMO energy of the NCMPs (both which influence the electron-donor ability) may preferentially direct the iodine adsorption capacity rather than surface area and pore size (determined by nitrogen adsorption at 77 K).<sup>66</sup> We used **P1**, **P2**, and **P3** as model compounds to monitor the HOMO energy of corresponding polymers on the basis of calculations at the B3LYP/6-31G (*d*) level with Gaussian 09 software.<sup>38</sup> **NCMP1**, with the highest nitrogen content, shows the highest HOMO energy (Table S9), which fits very well with the highest iodine adsorption capacity observed. Actual measurements of HOMO-LUMO band gaps for polymers were carried out using cyclic voltammetry (Figure S14) and UV-vis absorption scans (Figure 1c). The HOMO-LUMO band gaps ( $E_g$ ) of **NCMP1**, **NCMP2**, and **NCMP3** were calculated on the basis of the wavelengths at maximal UV-vis absorption ( $\lambda_{max}$ ) according to the equation:  $E_g = 1240/\lambda_{max}$ , giving values for  $E_g$  = 1.22, 1.17, and 1.54 eV, respectively. The results indicate that the electron-donating ability follows the order: **NCMP2** > **NCMP1** >> **NCMP3**, which is also seen in the strongest redox activity of **NCMP2** according to cyclic voltammetry measurements (Figure S14).

Previous studies showed that reduction and oxidization of secondary amine-linked HCMPs resulted in better iodine and CO<sub>2</sub> uptake capacities,<sup>20</sup> respectively. Owing to the similar molecular architectures of HCMPs and NCMPs, this conclusion should be also applicable to the NCMPs if the residual secondary amine moieties are mostly preserved. However, in stark contrast to the HCMP behavior reported before, the FT-IR spectra of **NCMP2** showed negligible changes except

for a weak peak at  $1630\text{ cm}^{-1}$  which is slightly increased when oxidized by  $\text{H}_2\text{O}_2$  or iodine and reduced by anhydrous hydrazine (Figure S15), respectively. This peak may be attributed to the small fraction of quinones existing in the conjugated polymer, which are sensitive to oxidation and reduction. The results indicate that a more stable structure is obtained for NCMPs compared to HCMPs. This is also supported by the negligible changes observed in the  $^{13}\text{C}$  NMR spectra of **NCMP2** upon oxidation and reduction (Figure S16). The treated porous polymers showed very small deviations in  $\text{CO}_2$  and iodine uptake capacities (Figs. S17 and Table S9). Meanwhile, five-point  $\text{N}_2$  adsorption measurements indicated that only a small decrease of surface area observed in **NCMP2** upon oxidization ( $256\text{ vs. }280\text{ m}^2/\text{g}$ ) is observed. These results prove that the small fraction of residual secondary amines, inevitably left in the polymers due to incomplete polymerization during network formation, are not sufficient to enable a polyaniline-like switching behavior. It can thus be concluded that the majority of secondary amines of the precursors has been converted into tertiary amines after polymerization. This is further confirmed by the finding that no methylene groups are detectable in NCMPs upon further reaction using diiodomethane as a cross-linker (note that such a cross-linking method has been well-developed for the leucoemeraldine base state of polyaniline<sup>30</sup>). Considering the polymers were purified using concentrated acid (35 wt% HCl) and hot water ( $75\text{ }^\circ\text{C}$ ) overnight, the results further indicate their high physicochemical stability.

Furthermore, NCMP networks with abundant tertiary nitrogen moieties possess the potential to coordinate metal ions and act as catalyst support. In an initial, proof-of-concept study, palladium dichloride ( $\text{PdCl}_2$ ) was coordinated to **NCMP2** (as **NCMP1** and **NCMP3** have either a lower specific surface area or lower nitrogen content, and were therefore not considered for this initial study). After  $\text{PdCl}_2$  was introduced, **NCMP2** showed a significant decrease in surface area from  $280\text{ to }26\text{ m}^2/\text{g}$  due to the weight gained by introducing Pd species and mainly pore blocking or so. Successful coordination was confirmed by ICP-AES, XRD, and XPS analyses as well as SEM and TEM observations. ICP-AES results showed that 11.8 wt% Pd (theoretical content: 21.3 wt%) and no Fe were present in the network structure. The XRD pattern of **NCMP2-PdCl<sub>2</sub>** shows four additional crystal reflections at  $2\theta = 39.9, 46.5, 68.2, \text{ and } 82.0^\circ$  (Figure 4a) owing to palladium particles,<sup>67</sup> indicating that the  $\text{PdCl}_2$  introduced was partially reduced to Pd(0). It has been reported

that electron-rich conjugated polymers with high N-content are able to reduce noble metal ions into metallic particles,<sup>68</sup> which seem to be the case also here. The XPS spectra confirm that C, N, Cl, Pd, and O are present in the **NCMP2-PdCl<sub>2</sub>** (Figure 4b). The O peak is possibly indicative of readily adsorbed oxygen or water, which is normally found in porous materials.<sup>69</sup> The Pd3d core-level XPS spectrum in Figure 5b shows two broad peaks at 337.2 and 342.4 eV, suggesting the existence of both Pd(0) and Pd(II) in the catalyst.<sup>70,71</sup> The result is consistent with that of recently reported Pd, N, P, and O-doped porous polymer catalysts.<sup>71</sup> The N1s core-level XPS spectrum of pristine **NCMP2** shows one binding energy at 399.7 eV owing to C-N bond of the NPh<sub>3</sub> moiety (Figure 5c). After PdCl<sub>2</sub> loading, it becomes less intense and a new signal at a binding energy of 400.1 eV appears (Figure 5d). This signal can be attributed to the PdCl<sub>2</sub>-coordinated NPh<sub>3</sub> moiety. SEM and TEM images indicate that the catalyst maintain the morphology of sphere-like nanoparticles after PdCl<sub>2</sub> impregnation (Figure 2b,e,h and Figure 7a,c), with some dark dots that show the additionally formed Pd nanoparticles.

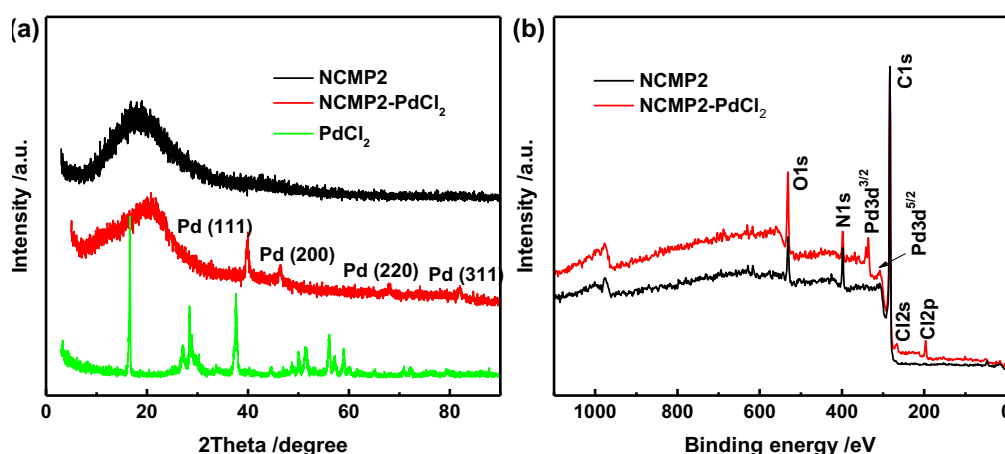


Figure 4 (a) Powder XRD patterns and (b) XPS survey spectra of **NCMP2** and **NCMP2-PdCl<sub>2</sub>**; PdCl<sub>2</sub> is showed for comparison.

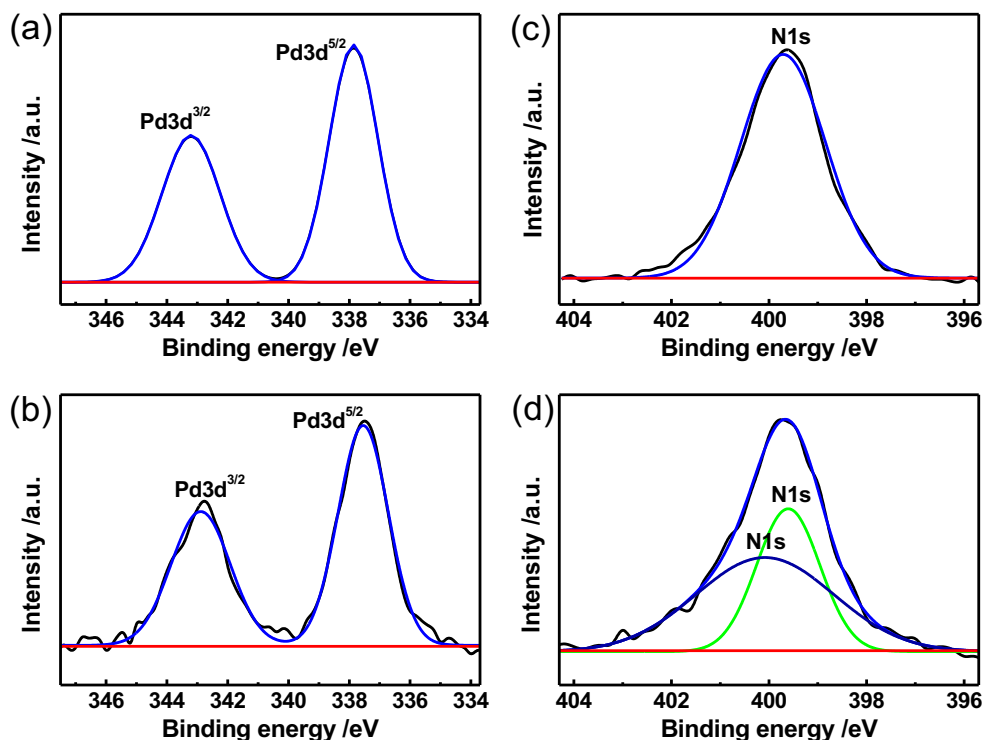
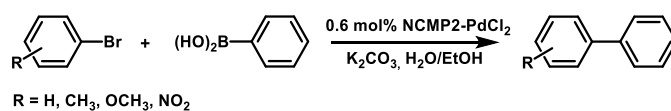
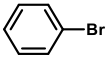
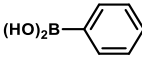
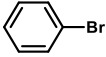
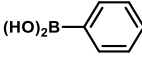
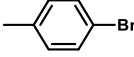
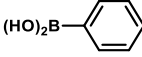
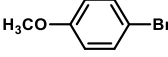
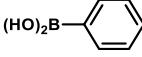
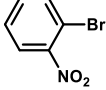
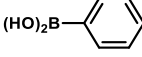
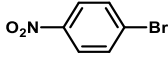
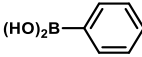
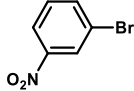
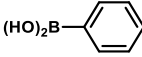


Figure 5 Pd3d (a,b) and N1s (c,d) core-level XPS spectra of (a) **PdCl<sub>2</sub>**, (c) **NCMP2**, and (b,d) **NCMP2-PdCl<sub>2</sub>** catalyst.

Applying **NCMP2-PdCl<sub>2</sub>** as a catalyst enables fast Suzuki–Miyaura coupling reactions in a 60% ethanol aqueous solution under mild conditions (80 °C). With a series of aryl bromides and benzenboronic acid used, biaryl products were obtained consistently in high yields (Table 2). The presence of additional Pd(0) nanoparticles within our NMCP materials could play a role and influence the catalytic performance of these materials, and would be valid grounds for further detailed studies into the catalytic behaviour of these complex systems. The **NCMP2-PdCl<sub>2</sub>** catalyst can be readily recycled by filtration and solvents washes. Applying phenyl bromide and benzenboronic acid as substrates, the recyclability tests show that the yields of the cross-coupling products remain >94% after six repeat reactions with the recycled catalysts (Figure 6, see supporting information for details of the procedure followed). Control experiments using pristine PdCl<sub>2</sub> as catalyst indicated no recyclability (although they showed catalytic activity close to that of the catalyst in presence of **NCMP2** in the first cycle).

Table 2 Suzuki–Miyaura coupling reaction catalyzed by **NCMP2-PdCl<sub>2</sub>**.



Entry	Substrate 1	Substrate 2	Reaction time	Yield
1 <sup>a</sup>			<0.5 h	99.9%
2			<0.5 h	99.9%
3			<0.5 h	99.4%
4			<0.5h	99.9%
5			<0.5h	95.1%
6			1 h	81.5%
7			1 h	65.3%

<sup>a</sup> Entry 1: control experiments were done using pristine PdCl<sub>2</sub> as the catalyst; Entries 2-7: experiments were done using **NCMP2-PdCl<sub>2</sub>** as the catalyst.

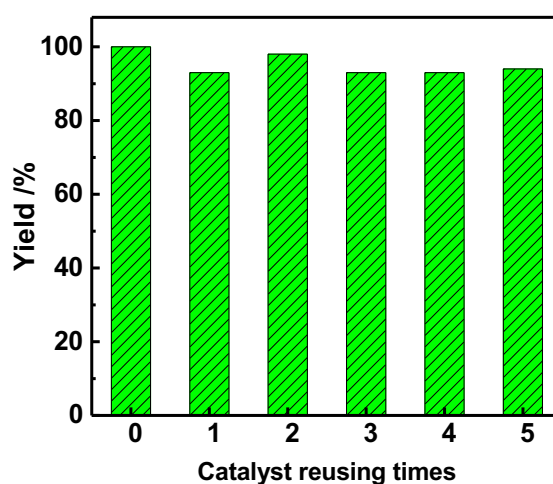


Figure 6 Product yields of Suzuki–Miyaura coupling reaction between phenyl bromide and benzenboronic acid (Entry 2) using **NCMP2-PdCl<sub>2</sub>** as a catalyst upon six continuous runs.

The recycled catalyst was also characterized using FT-IR, SEM, TEM, and TGA analyses. The SEM and TEM results showed that the catalyst maintained comparable chemical bonds and morphologies upon using 5 times, suggesting good stability (Figure 7a-d). Note that a strong and broad peak around  $3435\text{ cm}^{-1}$  due to water absorption is observed in both catalysts used before and after, as the measurements were carried out in a KBr pellet. TGA scans (under air) showed that the catalyst used before and after maintained a residue of  $\sim 10.5\text{ wt\%}$  when heated from  $540$  to  $900\text{ }^{\circ}\text{C}$ , indicating no substantial Pd species leaching occurred from the catalysts during long-term use.

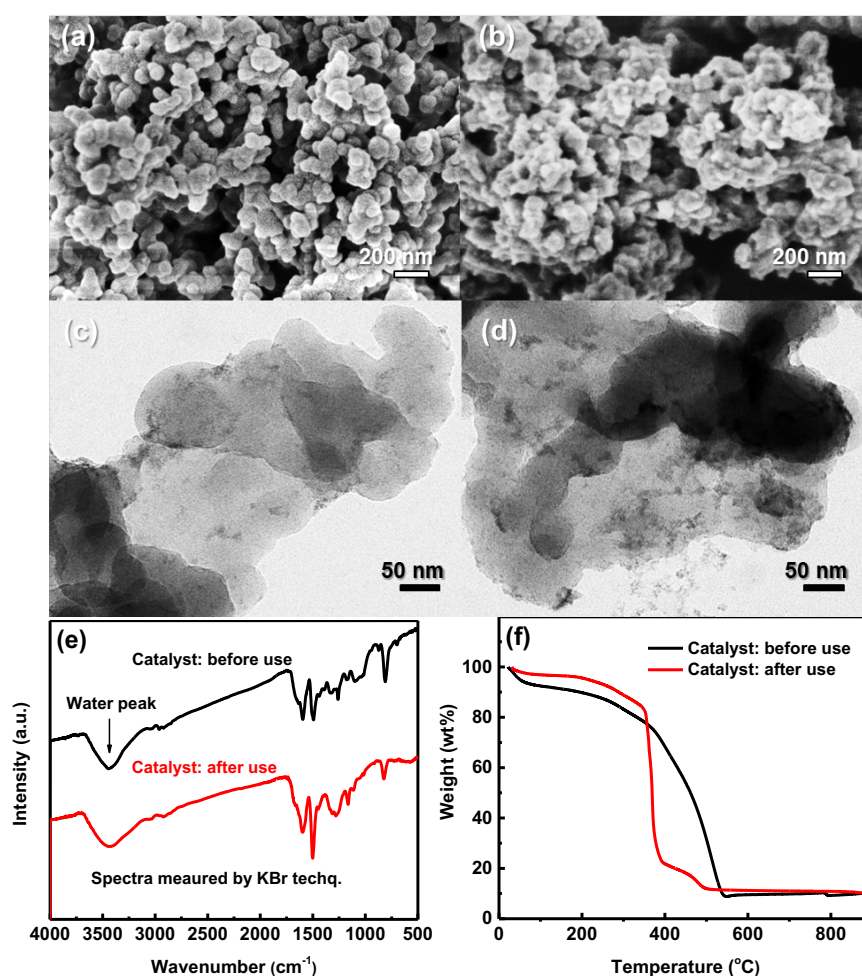


Figure 7 (a,b) SEM and (c,d) TEM images, (e) FT-IR spectra, and (f) TGA scans (under air) of **NMCP2-PdCl<sub>2</sub>** catalyst before (a,c) and (b,d) after used five times.

The catalytic activity and recyclability of **NMCP2-PdCl<sub>2</sub>** are competitive with the results recently reported for porous polymers supporting Pd catalysts.<sup>71</sup> Owing to the facile synthesis route, the cheap FeCl<sub>3</sub> oxidant involved in polymer synthesis and the high N-content, the here presented

NCMP2 is a convenient and attractive support for metal species.

## Conclusions

In summary, three nitrogen-rich conjugated microporous polymers (NCMPs), structurally close to well-known polyaniline, have been prepared at low cost using oxidative coupling of multi-connected aniline precursors. Optimizing molecular architectures of the NCMPs enables moderate CO<sub>2</sub>, H<sub>2</sub> and iodine storage abilities as well as good CO<sub>2</sub>-selectivity over N<sub>2</sub> at ambient pressure. Owing to their high nitrogen content and porosity, NCMPs can act as a suitable support for PdCl<sub>2</sub> coordination and, as a result, such supported catalysts show high activity and recyclability under mild conditions and aqueous reaction media for a model Suzuki–Miyaura coupling reaction. Following on from our investigations and results, we envisage that this functional and versatile family of materials will find future application in catalysis and related uses in the fields of gas and energy storage and conversion.

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## Supporting information

Experimental details, calculations for atomic electron spin density of the precursors and CO<sub>2</sub>/N<sub>2</sub> selectivity, FT-IR, TGA curves, additional CO<sub>2</sub> and H<sub>2</sub> adsorption isotherms, isosteric heat of CO<sub>2</sub> and H<sub>2</sub> adsorption, cyclic voltammetry scans, and summarized chemical/physical properties of NCMPs. Supporting information is available free of charge *via* the Internet at <http://pubs.acs.org>.

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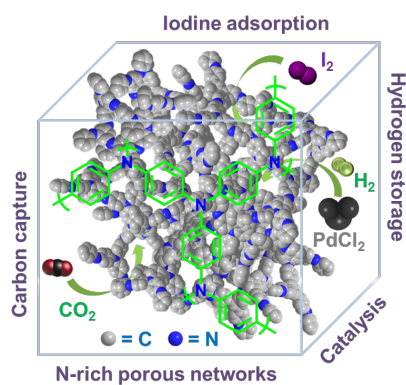
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### The table of contents entry



A chemical oxidative polymerization method for facile synthesis of N-rich conjugated microporous polymer networks with high N content and controllable surface area is developed. We demonstrate their use and application as adsorbents for efficient gas storage and recyclable catalyst supports.

**Title:** Nitrogen-Rich Conjugated Microporous Polymers: Facile Synthesis, Efficient Gas Storage and Heterogeneous Catalysis

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